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(54) Heat shrinkable co-extruded film and relevant preparation procedure.

(57) Three-layer heat shrinkable co-extruded film, the intermediate layer consisting of linear low density polyethylene or linear medium density polyethylene, added with hydrogenated hydrocarbon resins or other resins or low molecular weight polyethylene or polypropylene waxes, and the two external layers consisting of polypropylene or ethylene-propylene copolymer added with resins or waxes of the same group as used for the intermediate layer.

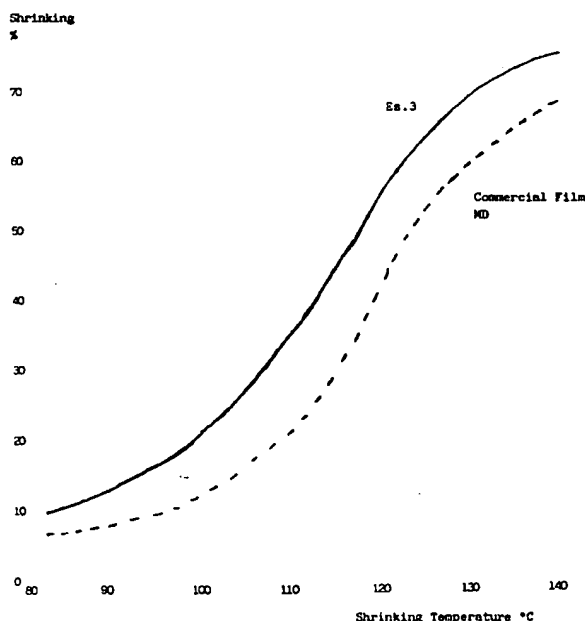


FIG. 1

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**Prior art**

The twin-bubble co-extrusion technique for the production of single-layer or multilayer heat shrinkable films is already known. The films thus obtained find application especially in the packaging sector.

- 5 For example, US patent 4,863,760 (Viskora) discloses the production of a heat shrinkable film, oriented by biaxial stretching in the two longitudinal and transversal directions, consisting of LLDPE (linear low density polyethylene) and  $\alpha$ -olefins.

Said film may be single-layer or co-extruded with mixtures containing EVA (ethylene-vinyl acetate copolymer) or LLDPE.

- 10 US patent 4,532,189 (Grace) discloses a three- or five-layer film whose intermediate layer consists of LLDPE or LMDPE (linear medium density polyethylene) added with EVA or EPC (ethylene-propylene copolymer) and whose external layers consist of EPC added with PP (polypropylene) or LLDPE.

This film shows a good tear strength as well as a good heat seal resistance.

The use of hydrocarbon resins to modify PP and EPC is also known.

- 15 European patent 00,210,750 (Hercules) claims the obtainment of an antistatic PP film, which may be heat-sealed at low temperature, starting from hydrocarbon resins.

Notwithstanding the good results brought about by the technique already known, the need of films of improved mechanical, optical, and heat sealing properties is felt, in particular in the packaging sector.

**20 Summary**

- It has surprisingly been found that a three-layer heat-shrinkable co-extruded film having improved characteristics can be obtained by mixing the three-layer constituent polyolefins with suitable additives and by operating under convenient conditions. The intermediate layer of said film consists of LLDPE (linear low density polyethylene) or LMDPE (linear medium density polyethylene) added with resins selected out of the group consisting of hydrogenated hydrocarbon resins, terpene resins, phenolic resins, pine resins, polycyclopentadiene, low molecular weight polyethylene or polypropylene waxes, VLDPE (very low density polyethylene), MA (maleic anhydride polymer), and AE (acrylic ester polymer), ethylene-acrylic ester-maleic anhydride terpolymer, EVA/MA (ethylene-vinylacetate-maleic anhydride terpolymer).

- 30 The two external layers of said film consist of PP (polypropylene) or EPC (ethylene-propylene copolymer) added with resins or waxes of the same group as used for the intermediate layer.

The procedure for the preparation of said film comprises the steps of

- a) mixing of the raw materials in granular form by traditional dry mixers to give the three mixtures for the three film layers to be obtained;
- 35 b) co-extruding the three mixtures fed to a die provided with three concentric annular slots;
- c) immediate cooling of the tubular film and heating of same by IR rays or hot air at a temperature close to the softening point;
- d) film orienting by twin-bubble biaxial stretching;
- e) film cooling by air blowing;
- 40 f) bubble cutting and film roll winding.

The film obtained according to the present invention exhibits improved characteristics of heat shrinking (%), mechanical resistance, stiffness, transparency and gloss.

**Detailed description of the invention**

- 45 The following detailed description sets forth the characteristics of and the advantages offered by the heat shrinkable co-extruded film as per the present invention and the relevant preparation procedure.

- The said film consists of three layers, the intermediate layer consisting of LLDPE (linear low density polyethylene) or LMDPE (linear medium density polyethylene) added with resins selected out of the group consisting of hydrogenated hydrocarbon resins, terpene resins, phenolic resins, pine resins, polycyclopentadiene, low molecular weight polyethylene or polypropylene waxes, VLDPE (very low density polyethylene), MA (maleic anhydride polymer) and AE (acrylic ester polymer) ethylene-acrylic ester-maleic anhydride terpolymer, EVA/MA (ethylene-vinylacetate-maleic anhydride terpolymer).

- 55 The two external layers of said film consist of PP (propylene homopolymer) or EPC (ethylene-propylene copolymer) added with resins or waxes of the same group as used for the intermediate layer.

The substances used have the following characteristics:

LLDPE and LMDPE consist of ethylene with 8% max. butene or octene or hexene or  $\alpha$ -methyl pentene; VLDPE consists of ethylene added with 10% max. octene and tetramethylpentene or propylene (density

0.890-0.910);

PP is a homopolymer of propylene having density of 0.90 approx. EPC is a copolymer consisting of ethylene and propylene, the latter being the major component;

hydrogenated hydrocarbon resins include hydrogenated aromatic hydrocarbon resins, hydrogenated terpene resins, etc., such as for example the resins obtained by hydrogenating resins produced by polymerization of various unsaturated aromatic hydrocarbons, e.g. styrene,  $\alpha$ -methylstyrene, vinyltoluene, vinylxylene, indene, ethyl and/or methyl indene, and terpene. This group also comprises the hydrogenated resins obtained by polymerization of fractions of petroleum cracking by-products with b.p. ranging from 150 °C to 300 °C. Polyethylene and polypropylene waxes have a molecular weight ranging from 1,800 and 8,000, are of emulsionizable type and may be oxidized or not oxidized.

The by wt. per cent amount of resins or waxes added to LLDPE or LMDPE for the intermediate layer ranges from 1.0 to 35.

The by wt. per cent amount of resins or waxes added to PP or EPC for the external layers ranges from 2 to 35.

The film preparation procedure comprises the following steps.

Proper proportions of the components in granular form (basic polymers and additives as required for each layer) are mixed.

The three feeders discharge the polymer into a single die provided with three concentric annular slots.

The melted polymer leaves the die as a 3-layer tubular film.

The tubular film, which is still hot, is sized by passing between an outer ring cooled by a liquid coolant, e.g. water at 15-30 °C, and an inner mould, which is also cooled by a liquid coolant, e.g. water at 15-30 °C.

The outer ring provides uniform cooling to the tubular film circumference. The max. temperature variation along the circumference is 1 °C.

By internal and external cooling the tubular film temperature drops from 210 °C approx. to 30 °C in 8-25 sec. The water leaving the outer ring adheres, as a liquid film, to the tubular film outer surface and flows to the chamber underneath.

In the next step, the tubular film is oriented by biaxial stretching in the two longitudinal and transversal directions by the twin-bubble technique comprising the following operations.

The cold tubular film is fed to an IR-ray or hot-air oven where it is heated to a temperature close to softening. The tubular film is inflated with compressed air and expanded in the transversal direction. This results in a transversal orientation of the molecules. At the same time, the tubular film is stretched in the longitudinal direction by causing the pull-roll upstream of the oven and the final pull-roll to operate at a different speed.

Once the film has undergone double hot stretching, it is rapidly cooled to stabilize the inner orientation of molecules.

Cooling is obtained by blowing air at 5 °C to 15 °C.

The operating conditions of primary tubular film cooling, sizing, bubble inflation, and film stabilization are basic features of the present invention claiming the production of a film with the desired characteristics.

The film obtained according to the claimed procedure is 8 to 60  $\mu$  thick and exhibits improved characteristics over the product obtained by the known technique.

In particular, the film of the invention exhibits:

- shrinking at 120 °C: from 41 to 53%
- mechanical resistance: from 100 to 150 N/mm<sup>2</sup>
- stiffness: from 500 to 700 N/mm<sup>2</sup>
- transparency: from 90 to 94%
- gloss: from 100 to 115 photoelectric cell units
- tearing propagation: from 12 to 18 g;
- shrinking strength: from 15 to 35 g/cm.

The shrinking vs. temperature curves plotted in Fig.1 show the transversal shrinking % of a product as per Example 3 in comparison with a commercial product (MD).

The improved physical and mechanical properties of the film bring about improved technological characteristics, i.e.:

- better orientation (higher % stretching at a lower temperature);
- better balancing in the two L and T (longitudinal and transversal) directions;
- lower shrinking strength even at high per cent shrinking;
- better adhesion between layers resulting in a higher heat seal resistance;
- better mechanical properties resulting from an excellent orientation;
- good optical characteristics.

Thanks to the above characteristics, the film as per the present invention is suitable for the packaging sector in general and in particular for the applications requiring a good film adhesion to the product (boxes, books, magazines, food, vegetables, and multiple packed products), in which sector it shows improved performance over the product of the prior art.

5 The following examples are conveyed by way of illustration, not of limitation.

#### EXAMPLE 1 (comparison)

10 A three-layer (A/B/A) film (where A stands for the external layers and B the intermediate layer) was prepared. Total thickness: 15  $\mu$ ; thickness of A: 2  $\mu$ ; thickness of B: 11  $\mu$ . Layers A consisted of propylene homopolymer (Moplen S 38 FT produced by HIMONT), melt index 1.8 (230°C, 2.15 kg), added with micronized silicon dioxide (0.5%) and a completely saturated hydrogenated hydrocarbon resin (2%) (molecular weight = 900 approx.; Brookfield viscosity = 1000 approx.).

The resin used was Eastotac H 130 produced by Eastman Kodak.

15 Layer B consisted of LLDPE (Dowlex NG 5056 produced by Dow Chemical), melt index 1 (190°C, 2.16 kg) and density 0.923. This polymer was added with 1% erucamide (sliding agent). In particular, Constab GL 6004 produced by Constab Co. was used. The temperature of the melted material leaving the die was 190°C approx. in the case of layer A and 200°C approx. in the case of layer B. The temperature of internal tubular film cooling water was 24°C, that of the external film coolant being 30°C. The tubular film leaving  
20 the die had a diameter of 180 mm. The film was then oriented in the transversal and longitudinal directions under the following conditions:

- temperature 170°C
- chamber pull-roll speed: 5 m/min
- oven pull-roll speed: 5.2 m/min
- 25 - winder pull-roll speed: 26 m/min
- inflated bubble diameter: 900 mm
- flat film width: 1415 mm.

The stretching ratio is therefore symmetrical:  $L \times T = 5 \times 5$ .

30 The film obtained as per the invention exhibits better characteristics than the film obtained according to the prior art. In particular:

- thickness is more uniform;
- shrinking percentage is higher and more balanced in the two directions L and T;
- tensile strength and elongation at break are higher;
- tear strength is higher.

35 The film characteristics are shown in Tables 1, 2, and 3.

#### EXAMPLE 2

40 The procedure of Example 1 was repeated using LMDPE instead of LLDPE for the intermediate layer, which, in addition, was added with 2% of hydrogenated hydrocarbon resin Eastotac H130.

LMDPE had melt index of approx. 1 (190°C, 2.16 kg) and density of 0.94.

The film characteristics are shown in Tables 1 and 3.

#### EXAMPLE 3

45 The procedure of Example 1 was repeated with minor modifications, i.e. the intermediate layer consisted of LLDPE added with 2% hydrocarbon resin, type Eastotac H 130 produced by Eastman Kodak.

The temperature of the melted material leaving the die was 190°C in the case of layer B and the bubble orientation temperature was 162°C approx.

50 The film characteristics are shown in Tables 1, 2, and 3. In particular, an improved adhesion between layers was found.

#### EXAMPLE 4

55 The procedure of Example 2 was repeated using, for the intermediate layer, LMDPE added with 4% hydrogenated hydrocarbon resin, type Eastotac H 130 produced by Eastman Kodak.

The film characteristics are shown in Table 1.

**EXAMPLE 5**

The procedure of Example 3 was repeated using, for the external layers, EPC, a random propylene-ethylene (ca. 5%) copolymer, having melt index of 3 to 4 (230 °C, 2.16 kg) and softening point, Vicat, of approx. 110 °C, added with 2% hydrocarbon resin Eastotac H130.

In particular, Moplen SYL 7008 produced by HIMONT was used.

The film characteristics are shown in Tables 1 and 2.

**EXAMPLE 6**

The procedure of Example 4 was repeated using, for the external layers, EPC, in particular Moplen SYL 7008 produced by HIMONT.

The film characteristics are shown in Table 1.

**EXAMPLE 7**

The procedure of Example 1 was repeated using, for the intermediate layer, a mixture of 100 parts LLDPE (type Dowlex NG 5056) and 10 parts VLDPE (type Teamex TMX 100 F of DSM) having density of 0.90 and melt index of 1.5.

The film characteristics are shown in Tables 1, 2, and 3.

**EXAMPLE 8**

The procedure of Example 7 was repeated using EPC for the external layers. In particular, Moplen SYL 7008 added with 2% Eastotac H 130 and 1% Constab GL 6001 was used.

The film characteristics are shown in Table 1.

**EXAMPLE 9**

The procedure of Example 1 was repeated using, for the intermediate layer, a mixture of LLDPE and an ethylene-acrylic ester-maleic anhydride terpolymer.

In particular, the mixture consisted of 100 parts LLDPE (Dowlex NG 5056) and 10 parts terpolymer (Lotader 2308 produced by Enichem Polimeri), having melt index of 2 (190 °C, 2.16 kg) and density of 0.94.

The film characteristics are shown in Table 1.

**EXAMPLE 10**

The procedure of Example 9 was repeated using EPC added with 2% Eastotac H130 for the external layers.

The film characteristics are shown in Tables 1, 2, and 3.

**EXAMPLE 11**

The procedure of Example 9 was repeated using, for the internal layer, a mixture of 100 parts LLDPE and 10 parts EVA-maleic anhydride terpolymer, in particular, DuPont's Bynel E 361 (melt index 1).

The film characteristics are shown in Table 1.

**EXAMPLE 12**

The procedure of Example 11 was repeated using EPC added with 2% of Eastotac H130 for the external layers.

The film characteristics are shown in Tables 1, 2, and 3.

**EXAMPLE 13**

The procedure of Example 5 was repeated by adding to the internal layer, in this example consisting of LLDPE Clearflex FG308 Enichem, a polypropylene wax having a density of 0.93 and a molecular weight of 4,500 in a ratio of 1.5% in the place of the hydrocarbon resin.

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A particular Epolene E43 wax (Eastam Chemical) was added.  
The film characteristics are shown in Table 1.

TABLE 1

Parameters measured	TEST	UNITS	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Light transmission	ASTM D 1033	%	94	94	92	92	92	92
Gloss	D 2457	photoelec. cell units	115	115	115	115	105	105
Shrinking at 120°C	-	%	L 40 T 46	44 50	44 52	43 50	45 51	45 51
Shrinking strength	D 2838	N/mm <sup>2</sup>	70	70	60	62	58	60
Elastic modulus	D 882	N/mm <sup>2</sup>	650	680	660	600	600	610
Tensile strength	D 882	N/mm <sup>2</sup>	120	125	120	105	115	118
Elongation at break	D 882	%	110	110	105	95	105	100
Tear strength	D 1938	g.	9	9	10	10	13	12

In all examples, film thickness is of 15 µ.

\* Reference commercial film Cryovac MD film (W.R. Grace)

TABLE 1 (cont. 'd)

	Parameters measured	TEST	UNITS	Ex.7	Ex.8	Ex.9	Ex.10	Ex.11	Ex.12	Ex.13	E*
5	Light transmission	ASTM D 1033	%	92	92	90	90	90	90	92	90
10	Gloss	D 2457	photoelec. cell units	110	105	110	105	110	105	105	100
	Shrinking at 120°C	-	%	L 47 T 51	48 51	47 50	48 51	48 53	49 53	50 55	45 50
15	Shrinking strenght	D 2838	N/mm <sup>2</sup>	73	67	80	90	90	86	60	105
	Elastic modulus	D 882	N/mm <sup>2</sup>	590	580	600	590	570	560	600	500
20	Tensile strenght	D 882	N/mm <sup>2</sup>	104	98	95	92	93	92	110	92
	Elongation at break	D 882	%	112	118	106	110	112	118	115	120
25	Tear strenght	D 1938	g.	17	16	14	17	14	18	15	11

TABLE 2 - Adhesion between layers

Test method (non-standardized). 20 mm wide strips were transversally cut from the extruded tubular film before inflation. After manual delamination of the internal layers, the force required for layers separation, starting from the delaminated ends was measured by a dynamometer.

	Ex.1	Ex.3	Ex.5	Ex.7	Ex.10	Ex.12	Ref.*
g	350	570	600	540	710	730	200

\*Ref. = reference coextruded film formed by layers consisting of propylene homopolymer/LLDPE/propylene homopolymer, obtained according to the procedure described in Example 1 but without hydrocarbon resins addition.

The improved adhesion between layers resulted in an improved heat seal resistance.

TABLE 3 - Heat seal resistance

The method (non-standardized) consisted in subjecting 200 mm  
wide heat-sealed film specimens to elongation at break test.

Heat-sealing was obtained by means of a hot wire or strap.

	Ex.1	Ex.2	Ex.3	Ex.7	Ex.10	Ex.12	E*
N/mm <sup>2</sup>	60	78	83	66	81	80	72

E\* Reference commercial film. Cryovac MD film (W.R. Grace)

### Claims

1. Three-layer heat-shrinkable coextruded film, the two external layers consisting of PP (polypropylene) or EPC (ethylene-propylene copolymer) added with resins selected out of the group consisting of hydrogenated hydrocarbon resins, terpene resins, phenolic resins, pine resins, polycyclopentadiene, low molecular weight polyethylene or polypropylene waxes, very low density polyethylene (VLDPE), maleic anhydride (MA) polymer, acrylic ester (AE) polymer, ethylene-acrylic ester-maleic anhydride terpolymer and EVA/MA terpolymer and the intermediate layer consisting of linear low density polyethylene (LLDPE) or linear medium density polyethylene (LMDPE) added with resins or waxes of the same group as used for the external layers.
2. The film according to claim 1 wherein said LLDPE and LMDPE consist of ethylene and 8% max. butene or octene or hexene or  $\alpha$ -methyl pentene.
3. The film according to claim 1 wherein said VLDPE consists of ethylene added with 10% max. octene and tetramethylpentene or propylene, having density of 0.890-0.910.
4. The film according to claim 1 wherein said PP is a propylene homopolymer having density of 0.90 approx.
5. The film according to claim 1 wherein said EPC is a copolymer consisting of ethylene and propylene, the latter being the major component.
6. The film according to claim 1 wherein the by wt. per cent amount of said resins or waxes added to PP or to EPC for the external layers ranges from 2 to 35.
7. The film according to claim 1 wherein the by wt. per cent amount of said resins or waxes added to LLDPE or to LMDPE for the intermediate layer ranges from 1.0 to 35.
8. The film according to claim 1 wherein shrinking at 120°C ranges from 41 to 53%, mechanical resistance from 100 to 150 N/mm<sup>2</sup>, stiffness from 500 to 700 N/mm<sup>2</sup>, transparency from 90 to 93%, gloss from 100 to 115 photoelectric cell units, tearing propagation from 12 to 18 g, shrinking strength from 15 to 35 g/cm.
9. Procedure for the preparation of a three-layer heat-shrinkable coextruded film wherein the two external layers consist of polypropylene (PP) or ethylene-propylene copolymer (EPC) added with resins selected out of the group consisting of hydrogenated hydrocarbon resins, terpene resins, phenolic resins, pine resins, polycyclopentadiene, low molecular weight polyethylene or polypropylene waxes, very low density polyethylene (VLDPE), maleic anhydride (MA) polymer and acrylic ester (AE) polymer, ethylene-acrylic ester-maleic anhydride terpolymer and EVA/MA terpolymer and the intermediate layer consists of linear low density polyethylene (LLDPE) or linear medium density polyethylene (LMDPE) added with resins or waxes of the same group as used for external layers, wherein



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- a) the raw materials are dry mixed to obtain the three mixtures for the three film layers to be obtained;
- b) the three mixtures are simultaneously extruded and fed to a die provided with three concentric annular slots;
- 5 c) the tubular film obtained is immediately cooled and then heated to a temperature close to softening;
- d) the tubular film is oriented by twin-bubble stretching;
- e) the film obtained is cooled by air blowing.
- 10 10. The procedure according to claim 9 wherein said tubular film is cooled by passing between an outer ring and an internal mould, both cooled by a liquid coolant at 15°C to 30°C, the max. temperature difference along the tubular film circumference being 1°C.
- 15 11. The procedure according to claim 9, wherein said tubular film cooling from 210°C to 30°C (step c) takes place in 8 to 25 sec.
12. The procedure according to claim 9, wherein said tubular film cooling is carried out by blowing air at 5°C to 15°C.

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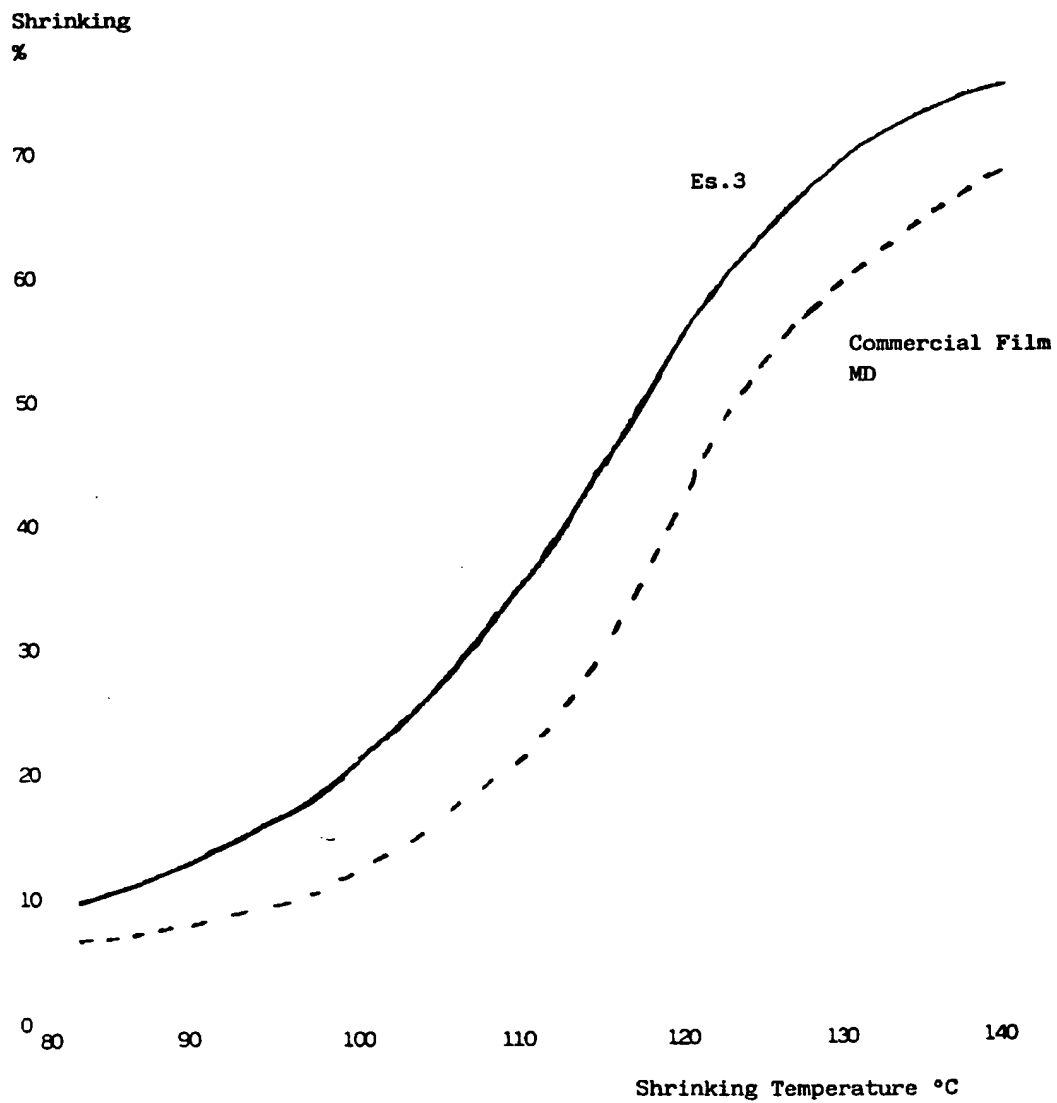


FIG. 1



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## EUROPEAN SEARCH REPORT

Application Number  
EP 93 11 7306

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
D,X	US-A-4 532 189 (W.R. GRACE & CO. CRYOVAC DIV.)	1-9	C08L23/04
Y	* column 7, line 19 - column 8, line 35; claims *	10-13	C08L23/10
	---		C08J5/18
A	EP-A-0 388 177 (W. R. GRACE & CO.)	1-9	B32B27/32
Y	* column 9, line 53 - column 10, line 37; claims *	10-13	
	---		
A	FR-A-2 635 312 (OKURA INDUSTRIAL)	1-13	
	* claims *		
	-----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C08L
			C08J
			B32B
			B24C
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		2 February 1994	Clemente Garcia, R
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